Effects of the generic nature of polymers on their fire behavior

Guy Marlair, A. Tewarson

EFFECTS OF THE GENERIC NATURE OF POLYMERS ON THEIR FIRE BEHAVIOR

G. Marlair
INERIS, Accidental Risks Division
Parc technologique ALATA, BP n°2, 60550 Verneuil-en Halatte, France
(Guy.marlair@ineris.fr)

A. Tewarson
Factory Mutual Research
1151 Boston-Providence Turnpike, Norwood, MA 02062, USA
(Archibald.Tewarson@fmglobal.com)

ABSTRACT

Fire behavior of four aliphatic and two aromatic C, H, O, N, S, and Cl atom containing polymers has been examined. Experiments were performed in three ASTM E 2058 Fire Propagation Apparatuses. The differences in the ignition behavior of polymers were found to be mainly due to differences in the ignition temperature. Chemical effects appear to contribute about 25 % towards the ignition resistance of the polymers. For thermoplastics, formation of polymer melt and its burning as a pool fire was found to increase the fire intensity by factors of two to four. The combustion efficiency and generation efficiency of CO_2 were found to decrease and the generation efficiencies of CO and smoke were found to increase by changes in the generic nature of the polymers (aliphatic to aromatic to halogenated). About four times as much carbon atoms in the polymers converted to smoke than converted to CO. Large-scale fire propagation behavior of polymers was characterized by a Fire Propagation Index (**FPI**). The **FPI** values of melting type thermoplastics (showing rapid-fire propagation behavior) were high, whereas they were low for the engineered charring type and halogenated polymers (showing either slow or decelerating fire propagation behavior).

KEYWORDS: flammability, fire properties, ignition, combustion, and fire propagation behaviors of generic polymers, release of heat, CO_2, CO and smoke, fire propagation apparatus

INTRODUCTION

Polymers are macromolecular organic materials manufactured by the modification of natural products or by synthesis from suitable intermediates. The number of basic polymers is large, the list is growing, and variations and modifications to these basic polymers, and co-polymers are quite large. Almost all the polymers consist of hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), chlorine (Cl), fluorine (F), and silicone (Si) atoms bonded alone or in combination with other atoms to the polymer backbone of carbon (C) atoms with different types of chemical bonding. Polymers can be predominantly crystalline, amorphous or a combination of both the natures. In predominantly crystalline polymers, chains are packed together more efficiently and tightly than in the amorphous polymers [1]. Polymers with higher crystallinity have higher thermal stability than amorphous polymers. All these differences are reflected in wide variations in the fire behavior of polymers.

In our study, we have attempted to examine the differences in the fire behavior of polymers because of variations in their generic nature and physical and chemical properties. Four aliphatic and two aromatic polymers with H, O, N, S, and Cl atoms bonded to the polymer backbone of C atoms were examined. Independent experiments were performed in the three ASTM E 2058 Fire Propagation Apparatuses [2], one at INERIS and two at the Factory Mutual Research (FMR).

EXPERIMENTAL

POLYMERS USED IN THE STUDY

The following polymers were examined as sheets from original resins, without any additives, except those used for processing:

1. Polyoxymethylene, POM (aliphatic: C, H, O atoms, M_{mono}: 29 g/mole, melting type);
2. Poly(methylmethacrylate), PMMA (aliphatic: C, H, O atoms; M_{mono}: 100 g/mole, melting type);
3. Nylon 6,6 (aliphatic: C, H, O, N atoms; M_{mono}: 226 g/mole, melting type);
4. Poly(vinylchloride), PVC, rigid (aliphatic: C, H, Cl atoms; M_{mono}: 62 g/mole, charring type),
5. Polycarbonate, PC (aromatic: C, H, O atoms; M_{mono}: 238 g/mole, charring type);
6. Polysulfone, PSF (aromatic: C, H, O, S atoms; M_{mono}: 442 g/mole, charring type).

The measured elemental composition and net heat of complete combustion are listed in Table 1. The data indicate that the resins are relatively pure with negligible amounts of impurities or additives. Additional information on the polymer samples, data analysis and experimental facilities are described in Ref [3]. For the analysis of experimental results, these data along with the literature data listed in Table 2 were used.

Table 1: Measured Elemental Composition and Net Heat of Complete Combustion of Polymers

Polymer	Elemental Composition (% weight)						H_T MJ/kg
	C	H	O	N	S	Cl	
Polyoxymethylene, POM	41.40	6.91	51.40	0.15	< 0.04	< 0.02	15.7
Polymethylmethacrylate, PMMA	60.10	8.56	32.14	<0.1	<0.04	<0.02	24.8
Nylon 6,6	61.86	10.25	17.82	11.98	<0.02	<0.02	29.2
Polyvinylchloride, PVC (rigid)	38.90	4.77	4.33	< 0.1	0.36	49.00	19.3
Polycarbonate, PC	75.70	5.50	18.40	< 0.1	< 0.04	< 0.02	29.9
Polysulfone, PSF	72.90	4.82	14.39	< 0.1	8.2	0.02	30.4

Table 2: Thermophysical Properties of Polymers from the Literature[a]

Polymers	$k \times 10^3$ (kW/m-K)	$\rho \times 10^{-3}$ (kg/m^3)	c (kJ/kg-K)	$\Delta H_{ch}/\Delta H_g$ (MJ/MJ)
POM	0.28	1.42	1.46	6
PMMA	0.18	1.19	1.47	17
Nylon 6,6	0.23	1.14	1.70	12
PVC (rigid)	0.25	1.38	1.41	2
PC	0.21	1.20	1.17	7
PSF	0.28	1.24	1.30	5

a: data are taken from Refs. 1,4,5,6,7, 8 and 9.

APPARATUS, EXPERIMENTS, AND MEASUREMENTS

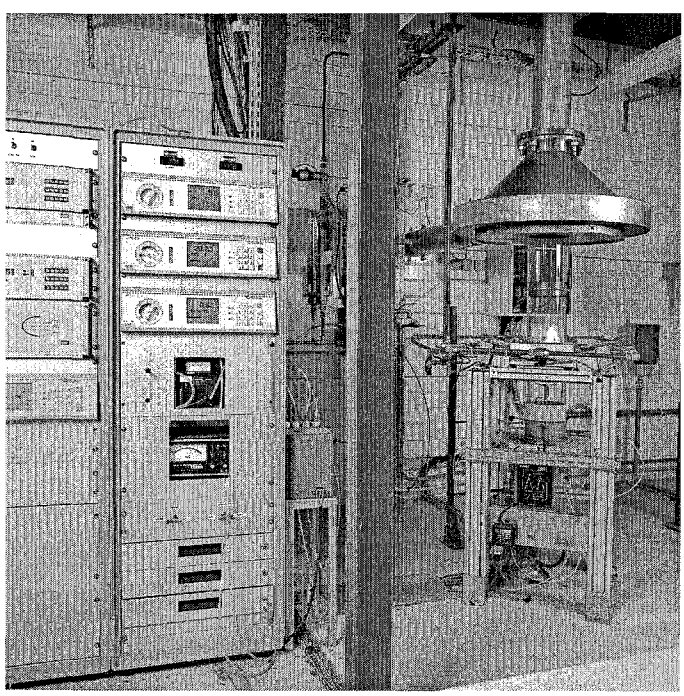

Figure 1. The INERIS Fire Propagation Apparatus [2]

One of the three ASTM E 2058 Fire Propagation Apparatuses used in this study is shown in Fig. 1. Three types of experiments were performed: 1) ignition, 2) combustion, and 3) fire propagation. For ignition and combustion experiments, 100-mm square and 10-mm thick horizontal sheets were used. The sample surface was painted black. For fire propagation experiments, 300-mm long, 100-mm wide and 10-mm thick vertical sheets were used. The sides and back of all the samples were tightly covered with ceramic paper and aluminum foil as described in the ASTM E 2058 standard. Cross wires across the surfaces were used for all the samples, because some of the samples expanded when exposed to external heat flux due to charring.

Ignition experiments were performed under quiescent normal airflow condition with a small pilot flame close to the surface. The entire sample surface was exposed to external heat flux in the range of 10 to 60 kW/m^2. Combustion experiments were performed under co-normal airflow rate of 158-mm/s (volumetric flow rate of 2.9 x 10^{-3} m^3/s) with

entire surface exposed to 50 kW/m^2 of external heat flux. The fire propagation experiments were performed in 40 % oxygen concentration in the co-air-oxygen mixture flowing at a rate of 158-mm/s (volumetric flow rate of 2.9 x 10^{-3} m^3/s). Only the 120-mm bottom part of the sample was exposed to 50 kW/m^2 of external heat flux in the presence of a pilot flame in the fire propagation experiments.

In the ignition experiments, ignition-time was measured as a function of the external heat flux. In the combustion and fire propagation experiments, measurements were made for the release rates of polymers vapors, heat, and products.

IGNITION

In the experiments, ignition-time, defined as the appearance of a sustained flame, was measured visually by a stopwatch. The measured ignition-time at each flux from the three laboratories varied between 3 to 15 % of the average value for the non-charring and non-expanding POM, PMMA, and nylon and between 4 to 31% of the average value for the charring and expanding PC, PSF, and PVC. The variations were higher at lower heat fluxes than for heat fluxes ≥ 30 kW/m^2, where the variations were only between 3 to 10% of the average value for all the polymers, a range used to obtain the ignition properties of the polymers.

The ignition-time and external heat flux relationship shown in Fig. 2 for POM is very similar for all the polymers and has been analyzed using the following well known relationship for thermally thick conditions [10,11]:

$$1/t_{ig}^{1/2} = (\dot{q}_e'' - \dot{q}_{cr}'')/(T_{ig} - T_a)\sqrt{k\rho c} \qquad (1)$$

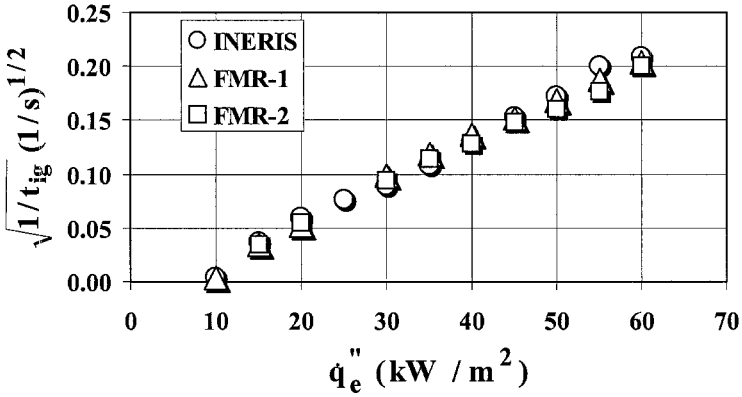

Figure 2. Relationship between ignition-time and external heat flux based on Eq. 1 and ignition data for POM measured in the ASTM E 2058 apparatuses.

The term $(T_{ig} - T_a)\sqrt{k\rho c}$ is defined as the *Thermal Response Parameter* (**TRP**) of the polymer [8]. $\dot{q}_{cr}''$ is the minimum heat flux at or below there is no sustained ignition, which is about 10 kW/m^2 in Fig. 2. The **TRP** value is derived from the inverse of the slope in the range of $\dot{q}_e'' \geq$ 30 kW/m^2. $\dot{q}_{cr}''$ and **TRP** values derived in this fashion are listed in Table 3.

The **TRP** values from the three laboratories vary between 6 to 11% of the average value. There is no variation in the $\dot{q}_{cr}''$ values. The values are lower for the aliphatic polymers compared to the aromatic and aliphatic halogenated polymers.

Data in Table 3 and for many polymers listed in the literature [1,4,5,6,7] show that the $\sqrt{k\rho c}$ component of **TRP** is approximately constant with an average value of 0.72 ± 19 %. The differences in the **TRP** values in Table 3 thus are mainly due to the differences in the T_{ig} values. This is supported by the estimated[1] $\sqrt{k\rho c}$ values also listed in Table 3, which are very similar to the calculated $\sqrt{k\rho c}$ values. The T_{ig} values of polymers depend on the chemical bond dissociation energies and generic nature of the polymer vapor in addition to thermal effects [9,12]. For ordinary polymers, $T_{ig} \approx$ vaporization (T_v) or decomposition temperature (T_d), which supports the influence of the bond dissociation energy on the ignition behavior [9,12]. For high temperature and highly halogenated advanced engineered polymers, $T_{ig} >> T_v/T_d$ suggesting the influence of both bond dissociation energy as well as of the generic nature of the polymer vapors [9,12]. It is estimated that chemical factors contribute to some 25 % in the **TRP** value [9].

[1] The $\sqrt{k\rho c}$ values of polymers were estimated from the expression: $\sqrt{k\rho c} = TRP/[\{(\dot{q}_{cr}'')^{0.25} x364\} - 293]$, where it is assumed that heat losses are mainly due to surface reradiation, polymer surface acts as a black body and the ambient temperature is 20 °C.

It is, therefore, necessary to account for factors such as energies associated with chemical bonds and chemical nature of the vapors in addition to thermal effects to describe the ignition behavior of polymers.

Table 3. Ignition Properties of Polymers

Polymer	Laboratory	TRP ($kW\text{-}s^{1/2}/m^2$)	$\dot{q}''_{cr}$ (kW/m^2)	$(k\rho c)^{1/2}$ ($kW\text{-}s^{1/2}/m^2\text{-}K$)	
				From Table 2	Estimated
POM (aliphatic C,H,O atoms)	INERIS	238	10	0.76	0.67
	FMR-1	286			0.81
	FMR-2	294			0.83
	Average	204 ± 11%		Average	0.77
PMMA (aliphatic C,H,O atoms)	INERIS	200	10	0.56	0.56
	FMR-1	196			0.55
	FMR-2	217			0.61
	Average	204 ± 6%		Average	0.58
Nylon 6,6 (aliphatic C,H,O,N atoms)	INERIS	263	15	0.67	0.62
	FMR-1	244			0.58
	FMR-2	278			0.66
	Average	262 ± 6 %		Average	0.62
PC (aromatic C,H,O atoms)	INERIS	323	25	0.54	0.62
	FMR-1	313			0.60
	Average	318		Average	0.61
PSF (aromatic C,H,O,S atoms)	INERIS	333	30	0.67	0.60
	FMR-1	357			0.64
	FMR-2	313			0.56
	Average	334 ± 7%		Average	0.60
PVC (aliphatic C,H,Cl atoms)	INERIS	333	15	0.70	0.79
	FMR-1	357			0.85
	FMR-2	385			0.91
	Average	358 ± 7%		Average	0.85

COMBUSTION

In the experiments, release rates of polymer vapors, heat, and fire products were determined[2]. In the experiments at 50 kW/m^2, the 10-mm thick melting type polymers (POM, PMMA, and nylon) burned as liquid pool fires, whereas the 10-mm thick charring type polymers (PVC, PC, and PSF) burned as solid polymers. Thus, the data for POM, PMMA, and nylon are for the combustion of polymer melts whereas the data for PVC, PC, and PSF are for the combustion of solid polymers.

The polymer vapors, heat and product release rate profiles and steady state (maximum) values from the three laboratories were in excellent agreement, such as shown by the data in Fig. 3 for the heat release profiles for POM and by the steady state data in Table 4 [3,4].

---

[2] For the determination of the heat release rate from the Oxygen Consumption (OC) and Carbon Dioxide Generation (CDG) Calorimetries, net heat of complete combustion per unit mass of oxygen consumed and CO and CO_2 generated were obtained from the data in Table 1.

[3] *Combustion efficiency* (χ) is defined as the ratio of the chemical (actual) heat of combustion to the net heat of complete combustion [8].

[4] *Generation efficiency* (f_j) of a product is defined as the ratio of the yield of the product to its maximum possible stoichiometric yield based on its elemental composition [8]. For example for the calculation of the maximum possible stoichiometric yield of CO, it is assumed that in the combustion all the carbon atoms in the polymer are completely converted to only CO.

Release Rates of Polymer Vapors, Heat, and Products

For the combustion experiments at $\dot{q}''_e = 50$ kW/m^2, the release rates of polymer vapors, heat, and products can be expressed as:

$$\dot{m}'' = (\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr})/\Delta H_g \quad (2)$$

$$\dot{Q}''_{ch} = (\Delta H_{ch}/\Delta H_g)(\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) = \chi(\Delta H_T/\Delta H_g)(\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) \quad (3)$$

$$\dot{G}''_j = (y_j/\Delta H_g)(\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) = f_j(\Psi_j/\Delta H_g)(\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) \quad (4)$$

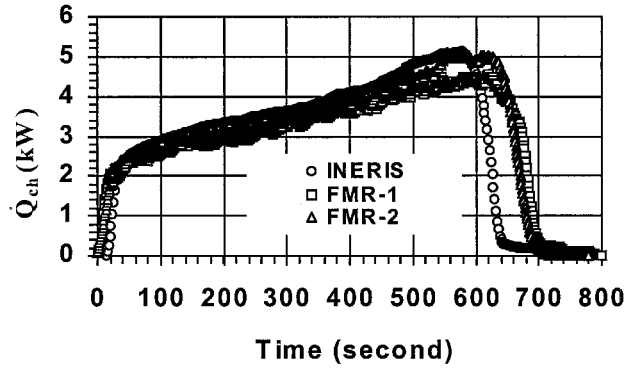

Figure 3. Heat release rate in the combustion of POM in normal air at 50 kW/m^2 in the ASTM E 2058 apparatuses.

In the combustion experiments, flames were completely lifted off the surface due to high release rate of polymer vapors. Under this condition, $\dot{q}''_f$ value can be assumed negligibly small and $\dot{m}''$ values can be predicted from $\Delta H_{ch}/\Delta H_g$ and $\dot{q}''_{rr}$ values. Assuming $\dot{q}''_f = 0$, the predicted $\dot{m}''$ values for ordinary polymers are in the range of about 20 to 30 x 10^{-3} kg/m^2-s for $\dot{q}''_e = 50$ kW/m^2. The measured range of $\dot{m}''$ values in Table 4 for the three charring type polymers (PVC, PC, and PSF) is similar to the predicted range. The measured range for $\dot{m}''$ values for melting type polymers (POM, PMMA, and nylon), however, is significantly higher than the predicted range for the solid polymers, but similar to that for the generic similar liquids. For example, the predicted $\dot{m}''$ values are 50, 55, 93 x 10^{-3} kg/m^2-s for methanol, hexadecane, and butanol respectively at 50 kW/m^2 [13].

The measured range of $\dot{m}''$ values for the melting type polymers (POM, PMMA, and nylon) are similar to the predicted $\dot{m}''$ range at 50 kW/m^2 for generically similar liquids. These observations suggest that formation, flow, and burning of polymer melt as liquid pool fires are critical stages in fires in thermoplastics (thickness ≤10-mm for $\dot{q}''_e \geq 50$ kW/m^2). The importance of these behaviors was also found critical in large-scale fires of 3 to 5-mm thick polymer parts of a minivan [14].

Combustion Efficiency and Generation Efficiency of Products

Data in Table 4 and Figs. 4 and 5 indicate that $\chi \approx f_{CO2}$, that these two parameters are inversely proportional to f_{CO} and f_{sm} and that there is a linear relationship between f_{CO} and f_{sm}. The data also show that χ and f_{CO2} decrease and f_{CO} and f_{sm} increase as the generic nature of the polymers changes from aliphatic to aromatic to halogenated. About four times as much carbon atoms are converted to smoke compared to the conversion to CO. Molecular weight of

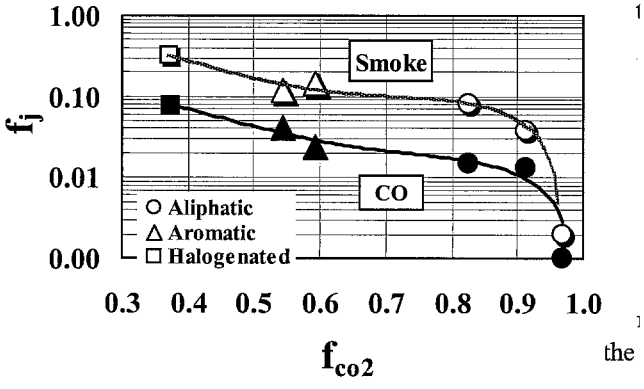

Figure 4. Relationship between the generation efficiencies of CO_2, CO, and smoke for the well-ventilated combustion of polymers.

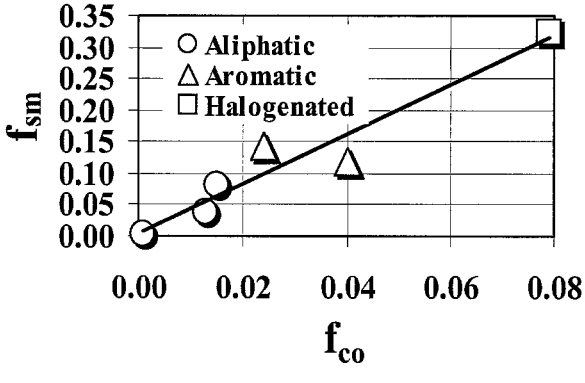

Figure 5. Relationship between the generation efficiencies of smoke and CO for the well-ventilated combustion of polymers.

of the atoms in the structure. The implications of variations in the χ, f_{CO2}, f_{CO} and f_{sm} values are reflected in the expressions for the release rates of heat and products in Eqs. 3 and 4.

Table 4. Release rates of Polymer Vapors and Heat, Heat of Combustion and Yields of Products in the Combustion of Polymers

Polymer	Laboratory	$\dot{m}''$ x 10^3 (kg/m^2-s)	$\dot{Q}''_{ch}$ (MW/m^2)	ΔH_{ch} (MJ/kg)	Yield (kg/kg)		
					CO	CO_2	Sm
POM aliphatic: C, H, O atoms M_{mono} = 29 g/mole	INERIS	52	0.75	15.1	0.002	1.46	0.001
	FMR-1	39	0.59	15.2	0.001	1.47	0.001
	FMR-2	43	0.66	15.4	0.001	1.49	0.001
	Average	44	0.67	15.2	0.001	1.47	0.001
	Combustion Efficiency			*0.97*			
	Generation Efficiency				*0.001*	*0.969*	*0.002*
PMMA aliphatic: C, H, O atoms M_{mono} = 100 g/mole	INERIS	84	1.81[a]	21.6[a]	(0.050)[a]	1.94[a]	0.022[a]
	FMR-1	80	1.83	23.0	0.012	2.02	0.030
	FMR-2	78	1.80	23.2	0.024	2.03	0.022
	Average	81	1.82	22.8	0.018	2.00	0.025
	Combustion Efficiency			*0.92*			
	Generation Efficiency				*0.013*	*0.912*	*0.038*
Nylon 6,6 aliphatic: C,H,O,N atoms M_{mono} = 226 g/mole	INERIS	46	1.21	23.8	0.026	2.04	0.037
	FMR-1	56	1.53	24.0	0.017	2.06	0.058
	FMR-2	54	1.54	25.0	0.029	2.14	b
	Average	52	1.43	24.3	0.024	2.08	0.048
	Combustion Efficiency			*0.83*			
	Generation Efficiency				*0.015*	*0.825*	*0.080*
PVC aliphatic: C,H,Cl atoms M_{mono} = 62 g/mole	INERIS	20	0.16	7.9	0.086	0.551	0.094
	FMR-1	21	0.17	8.2	0.071	0.570	0.128
	FMR-2	28	0.20	7.8	0.091	0.520	0.116
	Average	23	0.18	8.0	0.083	0.55	0.113
	Combustion Efficiency			*0.42*			
	Generation Efficiency				*0.079*	*0.372*	*0.323*
PC aromatic: C,H,O atoms M_{mono} = 238 g/mole	INERIS	23	0.43	18.9	0.046	1.73	0.117
	FMR-1	31	0.51	17.1	0.032	1.57	0.146
	FMR-2	28	0.49	18.3	0.049	1.67	0.086
	Average	27	0.48	18.1	0.042	1.66	0.116
	Combustion Efficiency			*0.60*			
	Generation Efficiency				*0.024*	*0.594*	*0.142*
PSF aromatic: C,H,O,S atoms M_{mono} = 442 g/mole	INERIS	20	0.44	17.2	0.045	1.59	0.098
	FMR-1	20	0.45	17.2	0.079	1.59	0.079
	FMR-2	22	0.39	16.5	0.085	1.52	0.085
	Average	21	0.43	17.0	0.070	1.57	0.087
	Combustion Efficiency			*0.56*			
	Generation Efficiency				*0.040*	*0.543*	*0.119*

a: slightly under-ventilated conditions due to extremely high burning rate at 50 kW/m^2. CO is unusually high and heat release rate, heat of combustion, and CO_2 and smoke yields are low; **b**: data not recorded properly.

FIRE PROPAGATION

Vertical fire propagation experiments were performed in 40 % oxygen concentration, with bottom 30 % of length exposed to 50 kW/m^2 in the presence of a pilot flame. The 40 % oxygen concentration simulates flame radiative heat

flux transferred to the surface in large-scale fires [15]. The fire propagation experiments thus are simulation of large-scale upward fire propagation.

In the experiments release rates of heat and products during upward fire propagation and initial and final weight of the sample were measured. Fire propagation was very rapid for POM and PMMA, but was slowfor PVC, PC, and PSF. Fire propagation experiments could be not be performed for nylon 6,6 due to rapid melting. The heat and product release rate profiles during fire propagation, from the three laboratories, were in excellent agreement, as shown in Fig. 6 for PMMA.

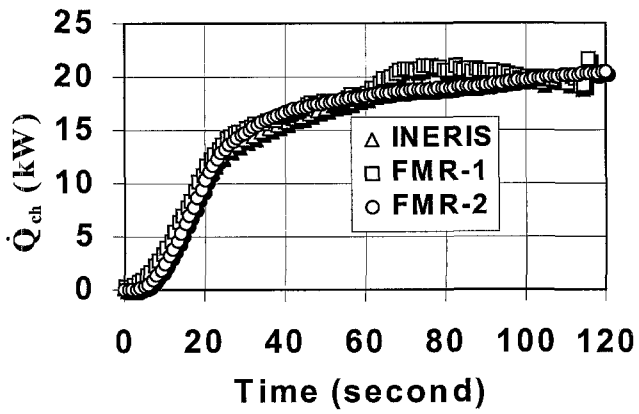

Figure 6. Heat release rate profile for the upward fire propagation at 40 % oxygen concentration for

For examining the upward fire propagation behavior of polymers, theoretical expression for the flame spread velocity [11,16,17,18] was utilized. With an assumption that the forward heat transfer from the leading edge of the flame is proportional to $(\dot{Q}/w)^n$, flame spread theories [11,16,17,18] suggest the following expression for the upward fire propagation velocity:

$$v^{1/2} \propto (\dot{Q}_r / w)^n /(T_{ig} - T_a)(k\rho c_p)^{1/2} \quad (5)$$

Based on the correlation between small-scale and large-scale upward fire propagation experiments, Eq 5 is modified as follows [19,20,21]:

$$v^{1/2} \propto [(\chi_r / \chi_{ch})\dot{Q}_{ch} / w]^{1/3} /(T_{ig} - T_a)(k\rho c_p)^{1/2} \quad (6)$$

Multiplying Eq. 6 by 1000 and assuming $\chi_r/\chi_{ch} \approx 0.42$, a *Fire Propagation Index* (**FPI**) has been defined to describe the large-scale vertical fire propagation behaviors of polymers based on small-scale test measurements [8,9,21]:

$$FPI = 1000\left(\frac{(0.42\dot{Q}_{ch} / w)^{1/3}}{(T_{ig} - T_a)(k\rho c)^{1/2}}\right) = 750\,(\dot{Q}_{ch} / w)^{1/3} /(T_{ig} - T_a)(k\rho c)^{1/2} \quad (7)$$

The $\dot{Q}_{ch}$ values from the fire propagation experiments and the $(T_{ig} - T_a)\sqrt{k\rho c}$ values, defined as **TRP**, from the ignition experiments are used in Eq. 7 to calculate the **FPI** values. Based on the visual observations in small-scale and large-scale fire propagation experiments, the following behaviors have been observed [8,9,19,20,21]:

- For FPI ≤ 6: flames are close to extinction conditions and fire propagation is limited to the ignition zone (area where surface is exposed to external heat flux in the presence of a pilot flame);
- For 6 < FPI≤ 10: fire propagation is decelerating and stops short of the sample length;
- For 10 <FPI≤ 20: there is fire propagation beyond the ignition zone;
- For FPI > 20: fire propagation beyond the ignition zone is very rapid.

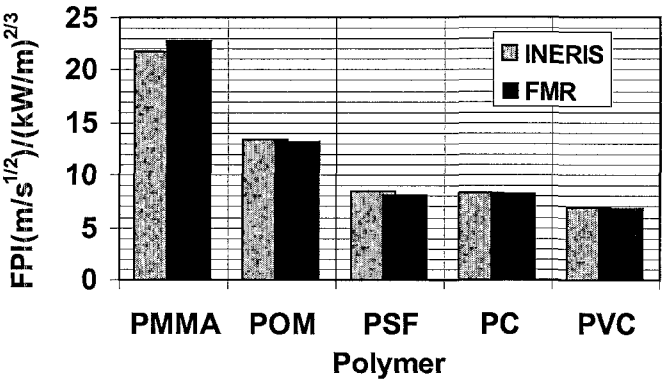

Figure 7 : Fire Propagation Indices of Polymers

Excellent correlation has been found between the **FPI** values from the small-scale and large-scale tests [8,9,19,21]. The **FPI** concept thus has been adopted for the acceptance of polymers in the clean rooms of the semi-conductor industry by Factory Mutual Research (FMR) and Underwriters Laboratories (UL) [22,23], and for electrical cables and conveyor belts by FMR [24,25]. Thus, we have also used the **FPI** concept in this study to describe the fire propagation behaviors of the selected polymers.

Since there is an excellent agreement between the three laboratories for the heat release

rate profiles and **TRP** values, **FPI** values from the three laboratories also show excellent agreement as indicated in Fig. 7.

The **FPI** value of PMMA (23) suggest rapid propagation that is confirmed by the data from the large-scale parallel tests [9,21] and many large-scale vertical wall fires [26,27,28,29]. The **FPI** value for POM is 13 for which fire propagation was observed to be rapid. For char forming polymers (PC and PSF) and halogenated polymer (PVC), the **FPI** values were in the range of 6.9 to 8.4, for which fire propagation was observed to be either slow or decelerating. Thus, all the factors that influence the variations in the ignition and combustion behaviors of polymers are also responsible for the differences in the fire propagation behavior.

SUMMARY

1) Under similar experimental conditions, differences in the ignition, combustion, and fire propagation behaviors of polymers are found to be influenced by the generic nature and molecular weight of the monomer;
2) Ignition temperature appears to be the main factor affecting differences in the ignition behavior of polymers. The $\sqrt{k\rho c}$ values are weakly dependent on the generic nature of the polymers. About 25 % of the ignition resistance is due to differences in the generic nature of the polymers;
3) The combustion efficiency and generation efficiency of CO_2 decrease and the generation efficiencies of CO and smoke increase as the generic nature of polymers changes from aliphatic to aromatic to halogenated. The combustion efficiency and generation efficiencies of products are closely related. A direct linear relationship is found between the generation efficiencies of CO and smoke, whereas an inverse non-linear relationship is found between the generation efficiency of CO_2 and that of CO and smoke;
4) About four times of the carbon atoms in the polymer are converted to smoke than to CO;
5) Generation rate of vapors for polymers that burn as solids is well predicted from the heat of gasification and surface reradiation loss at high external heat flux values where flame heat flux is negligibly small. The generation rate of vapors for polymers that burn as liquid pool fires however is under-predicted, suggesting that heat of gasification values for liquids rather than that of solid polymers need to be used.
6) Large-scale fire propagation behavior of polymers is well characterized by a Fire Propagation Index (**FPI**). Melting type ordinary thermoplastics have high **FPI** values and have been observed to have rapid-fire propagation. The **FPI** values for the engineered charring type and halogenated polymers are low and have been observed to have either slow or decelerating fire propagation beyond the ignition zone.

ACKNOWLEDGEMENTS

The financial support provided for this work (as part of the evaluation of the INERIS FPA) by the French Ministry for Land Use Planning and the Environment is gratefully acknowledged by one of us (GM).

NOMENCLATURE

$\mathbf{c}$	Heat capacity (kJ/kg-K)
$\mathbf{f_j}$	Generation efficiency of product j ($\mathbf{y_j/\Psi_j}$)
$\dot{\mathbf{G}}_{\mathbf{j}}''$	Generation rate of product j per unit polymer surface area (kg/m^2-s)
$\Delta\mathbf{H_{ch}}$	Chemical heat of combustion of the polymer (MJ/kg)
$\Delta\mathbf{H_g}$	Heat of gasification of the polymer (MJ/kg)
$\mathbf{k}$	Thermal conductivity (W/m-K);
$\dot{\mathbf{m}}''$	Release rate of polymer vapors per unit polymer surface area (kg/m^2-s)
$\mathbf{M_{mono}}$	Molecular weight of the monomer (g/mole)
$\mathbf{n}$	Number
$\dot{\mathbf{q}}_{\mathbf{i}}''$	Heat flux per unit polymer surface area (kW/m^2)
$\dot{\mathbf{Q}}_{\mathbf{ch}}''$	Chemical heat release rate per unit polymer surface area (kW/m^2)
$\mathbf{t_{ig}}$	Ignition-time (s)
$\mathbf{T}$	Temperature (°C)
$\mathbf{V}$	Upward fire propagation velocity (m/s)
$\mathbf{W}$	Sample width (m)
$\mathbf{y_j}$	Yield of product j (g/g)

Greek

χ	Combustion efficiency
ρ	Density (kg/m^3)
Ψ_j	Maximum possible mass stoichiometric yield of product j (g/g)

Subscripts

a	Ambient
cr	Critical
d	Decomposition
e	External
f	Fame
r	Radiative
rr	Re-radiation
T	Total or Complete
V	Vaporization

Superscripts

.	Per unit of time (1/s)
‘	Per unit width of the polymer
“	Per unit area of the polymer ($1/m^2$)

REFERENCES

1. Physical Properties of Polymers Handbook, J.E. Mark (Editor), American Institute of Physics, Woodbury, New York, 1996.
2. ASTM E 2058-00, "Standard Test Methods for Measurement of Synthetic Polymer Flammability Using a Fire Propagation Apparatus (FPA)", Annual Book of ASTM Standards 2000, Section 4 Construction, Volume 04.07, pp. 1084-1108. The American Society for Testing and Materials, West Conshohocken, PA. February 10, 2000 (also NFPA 287 National Fire Codes, Volume 6, pp. 287-1 to 287-28, National Fire Protection Association, Quincy, MA, 2000).
3. Marlair, G., and Tewarson, A., “Evaluation of the performance of three ASTM E 2058 and NFPA 287 Fire Propagation Apparatuses”, Interflam’01-Ninth International Fire Science and Engineering Conference (Proceedings pp. 1255 to 1260).
4. Domininghaus H., Plastics for Engineers-Materials, Properties, Applications. Hanser Publishers. New York, NY. 1988.
5. Abu-Isa, I.A., Cummings, D.R., and LaDue, D., “ Thermal Properties of Automotive Polymers I. Thermal Gravimetric Analysis and Differential Scanning Calorimetry of Selected Parts from a Dodge Caravan”, Report R&D 8775, General Motors Research and Development Center, Warren, MI, June, 1998.
6. Abu-Isa, I. A., “ Thermal Properties of Automotive Polymers II. Thermal Conductivity of Parts Selected from a Dodge Caravan”, Report R&D 8869, General Motors Research and Development Center, Warren, MI. US National Highway Traffic Safety Administration Docket Number NHTSA-1998-3588-39, March 29,1999.
7. Handbook of Plastics and Elastomers, Harper, C.A. (Editor), McGraw-Hill Book Company, New York, N.Y. 1975.
8. Tewarson, A., "Generation of Heat and Chemical Compounds in Fires", SFPE Handbook of Fire Protection Engineering, Section 3, Chapter 4, pp. 3-53 to 3-124. The National Fire Protection Association Press, Q-uincy, MA. 1995.
9. Tewarson., "Flammability of Polymers", Chapter 12 in Polymers and the Environment-A Handbook, A.L. Andrady (Editor), to be printed in 2002.
10. Delichatsios, M.A., Panogiotou, Th.P., and Kiley, F., "The use of time to ignition data for characterization the thermal inertia and minimum energy for ignition or pyrolysis", Combustion and Flame, **84,** 323-332, 1991.
11. Quintiere, J.G., "Surface Flame Spread", SFPE Handbook of Fire Protection Engineering, Section 2, Chapter 14, pp. 2-205 to 2-216. The National Fire Protection Association Press, Quincy, MA. 1995.

12. Tewarson, A., Abu-Isa, I.A., Cummings, D.R., and LaDue, D.E., "Characterization of the Ignition Behavior of Polymers Commonly used in the Automotive Industry", Fire Safety Science, Proceedings of the Sixth International Symposium, pp. 991-1002, University of Poitiers, France, 5-9 July, 1999. International Association for Fire Safety Science, ISBN 0-925-223-25-5, 2000.
13. Tewarson, A., "Flammability Properties of Engine Compartment Fluids Part I. Combustion Properties of Fluids Containing Carbon, Hydrogen, and Oxygen", Technical Report OB1R7.RC (1998), Factory Mutual Research, Norwood, MA. August 1998.
14. Ohlemiller, T.J., and Shields, J.R., "Burning Behavior of Selected Automotive Parts from a Minivan", Technical Report NISTIR 6143. National Institute of Standards and Technology, Gaithersburg, MD. August 1998. US National Highway Traffic Safety Administration Docket Number NHTSA-1998-3588-26, December 02, 1998.
15. Tewarson, A., Lee, J.L., and Pion, R.F., "The Influence of Oxygen Concentration on Fuel Parameters for Fire Modeling", Eighteenth Symposium (International) on Combustion, pp. 563-570. The Combustion Institute, Pittsburgh, PA. 1981.
16. Fernandez-Pello A.C., and Hirano, T., "Controlling Mechanisms of Flame Spread", Combustion Science and Technology, **32**, 1-31,1983.
17. Drysdale, D., An Introduction to Fire Dynamics, John Wiley and Sons, New York, NY. 1985.
18. Delichatsios, M.A., and Saito, K., "Upward Fire Spread: Key Flammability Properties, Similarity Solutions and Flammability Indices", Fire Safety Science-Proceedings of the Third International Symposium, pp. 217-226, Elsevier Applied Science, New York, NY. 1991.
19 Tewarson, A., and Khan, M.M., "Fire Propagation Behavior of Electrical Cables", Fire Safety Science-Proceedings of the Second International Symposium, pp. 791-800, Hemisphere Publishing Corporation, New York, NY. 1989.
20. Tewarson, A., and Khan, M.M., "Flame Propagation for Polymeric Materials in Cylindrical Configuration and Vertical Orientation", Twenty-Second Symposium (International) on Combustion, pp. 1231-1240. The Combustion Institute, Pittsburgh, PA. 1988.
21. Tewarson, A., Khan, M. M., Wu, P. K. S., and Bill, R. G., "Flammability of Clean Room Polymeric Materials for the Semiconductor Industry" J. Fire and Materials, **25**, 31-42, 2001.
22. FMR Test Standard 4910, "Clean Room Materials Flammability Test Protocol", Factory Mutual Research, Norwood, MA, September 1997.
23. UL 2360, "Standard Test Method for Determining the Combustibility Characteristics of Plastics Used in Semiconductor Tool Construction", Underwriters Laboratory, Northbrook, IL. 2000.
24. Specification Standard for Cable Fire Propagation, Class 3972, Factory Mutual Research, Norwood, MA, 1989.
25. Approval Standard, Class 1 Conveyor Belting, Class No. 4998, Factory Mutual Research, Norwood, MA, 1995.
26. Orloff, L., de Ris, J., and Markstein G., "Upward Turbulent Fire Spread and Burning of Fuel surfaces. Fifteenth Symposium (International) on Combustion, pp.183-192. The Combustion Institute, Pittsburgh, PA. 1974.
27. Orloff, L., Modak, A.T., and Alpert, R.L., "Burning of Large-Scale Vertical Plastic Surfaces", Sixteenth Symposium (International) on Combustion, pp.1345-1354. The Combustion Institute, Pittsburgh, PA. 1976.
28. Quintiere, J.G., Harkleroad, M,, and Hasemi Y., "Wall Flames and Implications for Upward Flame Spread", Combustion Science and Technology, **48**, 191-222, 1986.
29. Wu, P.K.S., and Tewarson, A., "Pyrolysis Efficiency in Upward Flame Spread", Interflam96-Seventh International Fire Science and Engineering Conference, pp. 159-168. St. John's College, Cambridge, U.K. Inerscience Communications Ltd., Greenwich, London, U.K. 1996.

Total number of words:	3663
Four Tables x 200:	800
Seven Figures x 200	1400
Total	5863